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(54) Title: FLEXIBLE POLYAMIDE FILM (57) Abstract The present invention provides flexible nylon films comprising, based on the total weight of the composition, from about 50 to about 95 weight % of a polyamide and from about 5 to about 50 weight % of a modified polyolefin having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides wherein the tensile modulus of a film formed from such composition is below about 85,000 psi (580 MPa) at 50 % relative humidity. Preferably, the modified polyolefin further comprises vinyl acetate.		

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FLEXIBLE POLYAMIDE FILM**5 BACKGROUND OF THE INVENTION****1. Field of Invention**

The present invention relates to improved
10 thermoplastic films. More particularly, this invention
relates to flexible polyamide films.

2. Description of Prior Art

15 Thermoplastic polymers that possess a range of useful
properties from stiffness and strength characteristics to
abrasion and chemical resistances are well known to the
art. Among these thermoplastic polymers are polyamides,
and the class of polyamides which are generally referred to
20 as nylons. Typically, most nylons are semi-crystalline in
structure, although chemically or thermally modified
amorphous polyamides can be produced. Nylons providing
useful physical properties have found utility in a broad
range of applications, including the formation of molded
25 articles, cast articles, blow molded articles, oriented and
non-oriented films, sheet, rods, fibers, fabrics, and
other.

Thermoplastic compositions comprising nylons have
30 found wide use in a film form for packaging in consumer and
industrial applications due to their advantageous
properties including chemical resistance, toughness,
strength, low gas permeability (including oxygen), and
relatively high heat stability that can readily be further
35 improved with an addition of traditional heat stabilizers,
such as metal halides.

In certain film applications, it is important that the
film conform to complicated shapes, and in such

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applications, the use of unmodified polyamide film has not been satisfactory due to the inherent stiffness of polyamides. Moreover, where such film applications require that the film be subjected to high temperature environments, the tendency of such unmodified nylon films to stiffen further when exposed to heat has discouraged their use. Such applications, including vacuum bagging or vacuum forming, would ideally require soft, flexible nylon films which exhibit satisfactory softness and good heat characteristics, while retaining good physical characteristics.

In order to provide such films, it has been known to the art to provide nylon film-forming compositions with plasticizers of various natures in attempts to provide such flexibility and softness to polyamide films. As is known to the art, incorporating plasticizers increases workability and flexibility of nylon films. However, prior attempts in utilizing plasticizers have produced films which have not been wholly satisfactory in particular applications. The addition of traditional low molecular weight plasticizers useful with polyamide resins, including sulfonamide and toluenesulfonamide plasticizers, has been known to lead to plating out of the plasticizers on chill rolls and formation of voids in the films due to thermal degradation of the plasticizer during the manufacturing process even when heat stabilizing additives are added to the film composition. Furthermore, the thermal degradation susceptibility of the low molecular weight plasticizers can cause degradation of the film when such film is utilized in high temperature applications.

The addition of high molecular weight polymeric plasticizers of the prior art, such as polyester adipate, polyester glutamate and polyester glycol, has not been

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satisfactory due to their thermal instability and incompatibility with polyamides. The compatibility of plasticizers with polyamides is far more critical in film compositions than in resin compositions since films, having
5 virtually a two-dimensional structure as the thickness dimension which is very small relative to their length and width dimensions, are far more sensitive to phase separations in their composition. Such phase separations must be avoided in order to ensure uniform chemical and
10 physical characteristics of the film. Traditionally, the need for a well mixed uniform composition, especially when one or more of the composition constituents are not readily miscible, was achieved by employing an additional manufacturing process known in the art as "master
15 batching." A master batching process comprises preparing a well mixed additive composition by extruding not-readily-miscible additives, such as plasticizers, with a relatively small amount of the major constituent of the film forming composition utilizing a high shear mixing extruder, or other
20 mixing device. Subsequently, the resulting composition, which is called a "master batch" in the art, is mixed and extruded with the rest of the composition constituents to form the final homogeneous film composition.

25 The unsatisfactory results in utilizing plasticizers designed for polyamide resins also arise from the fact that, unlike molded articles, films are subject to post-extrusion processes, such as orientation imparted by stretching the film. Therefore, nylon film forming
30 compositions are frequently subject to higher and longer heat exposure than resin compositions used for molding articles during manufacturing processes. In addition, nylon film manufacturing processes typically require higher processing temperatures and pressures than those of
35 manufacturing processes used for forming molded articles

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from such resins.

Accordingly, there remains a continuing need in the art for nylon films having good film softness and good heat characteristics, while retaining good physical characteristics. Therefore, it is desirable to have a plasticizer or a flexibility modifying agent that is thermally stable, compatible with the traditional heat stabilizer additives and highly compatible with polyamides such that the resulting film compositions are not susceptible to thermal degradation and phase separation. It is particularly desirable to have nylon film compositions with the above-mentioned good physical characteristics that form homogeneous compositions without having to utilize such extra processes as master batching process.

Furthermore, polyamides are generally hygroscopic, that is, they have a tendency to absorb moisture from their environment. Moisture acts as a plasticizer in polyamides, reducing most mechanical and electrical properties while changing flexibility and elongation characteristics. It is widely believed that water molecules actually replace the amide-amide hydrogen bond in polyamides with an amide-water hydrogen bond. The hygroscopic nature of polyamides further complicates the task of selecting appropriate plasticizers since the flexibility of polyamide film varies significantly with the humidity level of the surrounding environment. Therefore, it is further desirable to provide a plasticizer that can reduce the moisture sensitivity of polyamide film.

It is known in the art that various lactam monomers, such as caprolactam and lauryl lactam, can be added to film compositions in order to add softness and flexibility to films. However, since lactam monomers are highly volatile

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at elevated temperatures, they may be volatilized during the film manufacturing process in the form of fumes and may accumulate at various cold spots in the manufacturing equipment or in the manufacturing facility. Therefore, it is additionally desirous to utilize a plasticizer that is not volatile.

SUMMARY OF THE INVENTION

10 In accordance with the present invention, there is provided a flexible film comprising, based on the total weight of the composition, from about 50 to about 95 weight percent of a polyamide and about 5 to about 50 weight percent of a modified polyolefin having a functional moiety
15 selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides, wherein the tensile modulus of such film is below about 85,000 psi (580 MPa) at 50 percent relative humidity. Preferably, the modified polyolefin further comprises from about 3 to about
20 40 weight % of vinyl acetate.

In a further aspect of the invention there is provided an improved nylon film having a generally homogeneous structure which film exhibits improvements in softness and
25 film flexibility.

In a yet further aspect of the invention there is provided an improved nylon film which exhibits reduced moisture sensitivity.

30

In a yet further aspect of the invention there is provided an improved nylon film which retains softness and flexibility when subjected to a heat ageing process.

35 In a still further aspect of the invention there is

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provided an improved nylon film which exhibits low volatilization during the production and the utilization of the film.

5 These and other aspects of the present invention will become more apparent from the following disclosure.

**DETAILED DESCRIPTION OF THE INVENTION
AND PREFERRED EMBODIMENTS**

10

The present invention provides flexible nylon films comprising from about 50 to about 95 weight %, more preferably about 60 to about 90 weight %, and most preferably about 65 to about 85 weight %, of a polyamide
15 and, correspondingly, from about 5 to about 50 weight %, more preferably about 10 to about 40 weight %, and most preferably about 15 to about 35 weight %, based on the total weight of the composition, of a modified polyolefin having a functional moiety selected from the group
20 consisting of unsaturated polycarboxylic acids and acid anhydrides, wherein the tensile modulus of the film is below about 85,000 psi (580 MPa) at 50% relative humidity. Preferably, the modified polyolefin further comprises from about 3 to about 40 weight %, more preferably about 4 to
25 about 30 weight %, and most preferably about 5 to about 25 weight %, based on the total weight of the modified olefin, of vinyl acetate.

Polyamides, commonly known as "nylons," suitable for
30 the present invention include those which may be obtained by the polymerization of a diamine having two or more carbon atoms between the amine terminal groups with a dicarboxylic acid, or alternately those obtained by the polymerization of a monoamino carboxylic acid or an
35 internal lactam thereof with a diamine and a dicarboxylic

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acid. Further, suitable polyamides may be derived by the condensation of a monoaminocarboxylic acid or an internal lactam thereof having at least two carbon atoms between the amino and the carboxylic acid groups, as well as other means. General procedures useful for the preparation of polyamides are well known to the art, and the details of their formation are well described, for example, under the heading "Polyamides" in the Encyclopedia of Chemical Technology published by John Wiley & Sons, Inc, Vol. 18, pps.328-436, (1984).

Suitable diamines include those having the formula



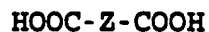
15

wherein n preferably is an integer of 1 - 16, and includes such compounds as trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, and hexadecamethylenediamine; aromatic diamines such as p-phenylenediamine, m-xylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenylmethane, alkylated diamines such as 2,2-dimethylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, and 2,4,4-trimethylpentamethylenediamine, as well as cycloaliphatic diamines, such as diaminodicyclohexylmethane, and other compounds.

30

The dicarboxylic acids useful in the formation of polyamides are preferably those which are represented by the general formula

35



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wherein Z is representative of a divalent aliphatic radical containing at least 2 carbon atoms, such as adipic acid, sebacic acid, octadecanedioic acid, pimelic acid, subeic acid, azelaic acid, undecanedioic acid, and glutaric acid; or a divalent aromatic radical, such as isophthalic acid and terephthalic acid.

By means of example, suitable polyamides include:

polypropiolactam (nylon 3), polypyrrolidone (nylon 4),
 10 polycaprolactam (nylon 6), polyheptolactam (nylon 7),
 polycaprylactam (nylon 8), polynonanolactam (nylon 9),
 polyundecaneolactam (nylon 11), polydodecanolactam (nylon 12),
 poly(tetramethylenediamine-co-adipic acid) (nylon 4,6),
 poly(tetramethylenediamine-co-isophthalic acid) (nylon 4,I),
 15 polyhexamethylenediamine adipamide (nylon 6,6),
 polyhexamethylene azelaamide (nylon 6,9),
 polyhexamethylene sebacamide (nylon 6,10),
 polyhexamethylene isophthalamide (nylon 6,I),
 20 polyhexamethylene terephthalamide (nylon 6,T),
 polymetaxylene adipamide (nylon MXD:6), poly
 (hexamethylenediamine-co-dodecanedioic acid) (nylon 6,12),
 poly(decamethylenediamine-co-sebacic acid) (nylon 10,10),
 poly(dodecamethylenediamine-co-dodecanedioic acid) (nylon 12,12),
 25 poly(bis[4-aminocyclohexyl]methane-co-dodecanedioic acid) (PACM-12), as well as copolymers of the above polyamides. By way of illustration and not limitation, such polyamide copolymers include: caprolactam-hexamethylene adipamide (nylon 6/6,6), hexamethylene
 30 adipamide-caprolactam (nylon 6,6/6), hexamethylene adipamide/hexamethylene-isophthalamide (nylon 6,6/6IP), hexamethylene adipamide/hexamethylene-terephthalamide (nylon 6,6/6T), trimethylene adipamide-hexamethylene-azelaamide (nylon trimethyl 6,2/6,2), and hexamethylene
 35 adipamide-hexamethylene-azelaamide caprolactam (nylon

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6,6/6,9/6) as well as others polyamide copolymers which are not particularly delineated here. Blends of two or more polyamides may also be employed.

5 The preferred polyamides suitable for use in the present invention are polycaprolactam (nylon 6), polyhexamethylene adipamide (nylon 6/6), and copolymers and blends thereof. Preferably, the caprolactam-based polyamides suitable for use in the present invention
10 exhibit a number average molecular weight, which is determined by the formic acid viscosity method, of between about 10,000 and about 60,000; more preferably, the polyamides exhibit a number average molecular weight of between about 15,000 and about 45,000.

15

 In accordance with the present invention, a further constituent in the film of the present invention is a modified polyolefin. The modified polyolefin comprises from about 5 to about 50 weight %, more preferably about 10
20 to about 40 weight %, and most preferably about 15 to about 35 weight %, of the total weight of the film composition.

 The polyolefins which may be used to form the modified reaction product suitable for the present invention include
25 crystalline or crystallizable poly(α -olefins) and their copolymers, wherein the α -olefin monomers have between about 2 and about 6 carbon atoms. Non-limiting examples of suitable polyolefins include low, medium or high density polyethylene, linear low density polyethylene,
30 polypropylene, polybutylene, polybutene-1, polypentene-1, poly-3-methylbutene-1, poly-4-methylpentene-1, polyhexene, and copolymers and blends thereof. Of these, preferred polyolefins are polyethylenes, polypropylene, polybutylene, and copolymers and blends thereof.

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- 10 -

The modified polyolefins suitable for use in conjunction with the present invention include copolymers and graft copolymers of a polyolefin and a constituent having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof. The unsaturated polycarboxylic acids and anhydrides include maleic acid, maleic anhydride, fumaric acid, crotonic acid, citraconic anhydride, itaconic anhydride and the like. Preferred of these are anhydrides, of which the most preferred is maleic anhydride.

The preferred modified polyolefin comprises between about 0.001 and about 10 weight % of the functional moiety, based on the total weight of the modified polyolefin, having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof. More preferably, the functional moiety comprises between about 0.005 and about 5 weight %; most preferably, between about 0.01 and about 2 weight %.

The modified polyolefins suitable for the present invention can be produced in accordance with the processes known to the art, including but not limited to the processes described in U.S. Patent Nos. 3,481,910; 3,480,580; 4,612,155 and 4,751,270. In performing the graft-polymerization of unsaturated carboxylic acid and anhydride to polyolefin, there have been utilized various methods for initiating the grafting polymerization process such as γ -ray, X-ray or high-speed cathode ray irradiation processes, and a free radical initiator process. The reaction of the polyolefin with an unsaturated polycarboxylic acid or an anhydride in the presence of a free radical (e.g., a peroxide) is the most widely used method of the grafting process. The method of using peroxide is advantageous since no special equipment or

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device is required for initiating the graft polymerization reaction although the method suffers from non-specificity and less than optimal grafting efficiency. Examples of the peroxides employable include benzoyl peroxide, tert-butyl peroxybenzoate, cumene hydroperoxide and azo compounds, such as azo-bis(isobutyronitrile). U.S. Patent No. 4,612,155 discloses a grafting process employing such a radical initiator that obtains the grafting yield of 50-90% under favorable circumstances. U.S. Patent No. 4,751,270 discloses more specialized radical initiators that attain up to 100% grafting efficiency and improve grafting specificity of the functional moiety to polyolefins.

Graft polymerization reaction is generally performed by standard graft polymerization techniques known in the art, such as heating a mixture of a polyolefin, a monomer of the functional moiety and a radical initiator, after mixing those or in mixing procedure, to a temperature at which polyolefin becomes molten, under kneading of the mixture. Alternatively, the above-stated compounds are dissolved or suspended in an appropriate solvent to perform the graft polymerization reaction.

The modified polyolefin of the present invention preferably further comprises between about 3 to about 40 weight %, based on the total weight of the modified polyolefin, of vinyl acetate. More preferably, the modified polyolefin comprises between about 4 and about 30 weight % of vinyl acetate; most preferably, between about 5 and about 25 weight %.

The modified polyolefins suitable for use in the present invention may also contain at least one thermoplastic elastomer such as ethylene/propylene rubber, ethylene/1-butene rubber, butyl rubber, butadiene rubber,

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styrene/butadiene rubber, ethylene/butadiene rubber, isopropene rubber, isobutylene or the like. Preferred thermoplastic elastomers are ethylene/propylene rubber and isobutylene rubber. Such thermoplastic elastomers may also
5 be modified with a constituent having a functional moiety selected from the group consisting of unsaturated polycarboxylic acids and acid anhydrides thereof in accordance with the method described above in conjunction with modified poly(α -olefin).

10

The compositions of the present invention may also include one or more conventional additives which do not materially affect the physical properties of the films including: lubricants, heat stabilizers, coloring agents
15 including dye and pigments, flame-retardants, fibrous and particulate fillers and reinforcing agents (both organic and inorganic), nucleators, ultraviolet light stabilizers, as well as other additives. These conventional additives may be incorporated into compositions at any suitable stage
20 of the production process; typically such conventional additives are included in the mixing step and included in an extrudate.

The film compositions of the present invention may
25 contain one or more heat stabilizers which include Group I metal halides, e.g., sodium, potassium, and lithium with cuprous halides, e.g., chloride, bromide, iodide; hindered phenols; hydroquinones, and varieties of substituted members of those groups and combinations thereof.

30

As another optional constituent, the film compositions of the present invention may further comprise a coloring agent, which agent may be a dye, pigment or other coloring agent or material which is useful in imparting a color
35 modification to the noncolored nylon, and which are not

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found to have a detrimental effect on the film compositions, particularly subsequent to heat ageing. Useful coloring agents include those which are known to the art as suitable for coloring polyamide comprising
5 compositions and generally include inorganic pigments, metal oxides, organic pigments, organic dyes, as well as other coloring agents and color concentrates known to the art.

10 Blending or mixing of the constituents which comprise the film compositions may be accomplished by any effective means which will effect their uniform dispersion. All of the constituents may be mixed simultaneously or separately
15 utilizing the mixing means well known in the art, such as a mixer or extruder. A common method is to melt-knead a previously dry-blended composition further in a heated extruder provided with a single-screw, or in the alternative, a plurality of screws, extrude the uniform composition into strands, and subsequently chop the
20 extruded strands into pellets. In an alternative and a preferred method, the dry-blended composition is provided to a film forming apparatus which comprises a heated extruder having at least a single screw. The heated extruder melt-blends the film composition and forms a film
25 therefrom. This method is generally to be preferred as it provides an overall reduction of process and handling steps necessary to form a useful film combination therefrom.

The film compositions of the present invention may be
30 formed into films by conventional methods using conventional film forming apparatus. Conventional methods include the production of films by blown film techniques, by extruding the film through a film forming die and optionally casting the film, calendaring, and forming a
35 film forming composition into a billet and subsequently

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skiving a film from the billet. In one of these methods, a film forming composition is plasticized and melt blended in an extruder to form an extrudate, which extrudate is then heated and extruded through a film forming die and then transported to a casting roll. In another method, the film forming apparatus may be one which is referred to in the art as a "blown film" apparatus and includes a circular die head through which the plasticized film composition is forced and formed into a film "bubble", which is ultimately collapsed and formed into a film.

The films may optionally be stretched or oriented in any direction if so desired. In such a stretching operation, the film may be stretched in either the direction coincident with the direction of movement of the film being withdrawn from the casting roll, also referred to in the art as the "machine direction", or in a direction which is perpendicular to the machine direction, and referred to in the art as the "transverse direction", or in both the machine direction and the transverse direction, where the resulting film is considered to be "biaxially" oriented.

The films formed by any of the above methods may be of any thickness desired and includes those which have thicknesses typically less than 20 mils (500 μm). Preferably, the films have a thickness in the range of about 0.1 mil (2.5 μm) and about 10 mils (250 μm); most preferably the films have a thickness of between about 1 mil (25 μm) and 5 mils (125 μm). While such thicknesses are preferred as providing a readily flexible film, it is to be understood that other film thicknesses may be produced to satisfy a particular need and yet fall within the present invention's scope.

- 15 -

In general, the flexible and conforming properties of the film of the present invention may be characterized as having low tensile modulus, low yield strength, high yield elongation and high ultimate elongation. Particularly, low
5 tensile modulus indicates flexibility of the film. Accordingly, the flexible film of the present invention preferably has tensile modulus below about 85,000 psi (580 MPa) at 50% relative humidity. Most preferably, the flexible film has tensile modulus below about 75,000 psi
10 (510 MPa) at 50% relative humidity.

It has been found that the films of the present invention provide good retention of physical properties, such as flexibility, softness and conforming
15 characteristics, and feature low embrittlement even when subjected to high heat for an extended duration. In addition, the films of the present invention do not have any significantly volatile constituents and are not as moisture sensitive as the flexible nylon films of the prior
20 art. Furthermore, it has unexpectedly been found that the film compositions of the present invention form non-phase separating homogeneous mixtures that do not require additional mixing steps or pre-blending processes, such as master batching, due to the high compatibility of the
25 plasticizers of the present invention with polyamides.

The flexible, soft and relatively heat-stable films of the present invention find particular utility in the formation of parts or articles, particularly composite
30 parts and articles. Typically, the formation of the article requires that a "preform" of the article, which contains one or more layers of an organic or inorganic web that is impregnated with an at least partially uncured resin, is wrapped in a film, and the wrapped preform is
35 then subjected to elevated temperatures for a period of

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time, usually in excess of one hour. The films of the present invention provide good flexibility which readily conforms to complicated or complex preform shapes, and further feature excellent retention of physical properties subsequent to the heat ageing conditions and pressure normally associated with vacuum bagging and vacuum forming operations.

Several examples are set forth below to illustrate the nature of the invention and the manner of carrying it out. However, the invention should not be considered as being limited to the details thereof.

EXAMPLES

15

In the following examples, it is to be understood that all references to a percentage of a constituent in a composition are the weight percentage of the referenced constituent relative to the total weight of the composition and that the physical properties of the examples were tested in the machine direction since the samples of the machine direction are less susceptible to the effects of flaws in the film casting dies and other film processing equipments.

25

Example 1-4

Examples 1-4 were formed from the constituents indicated in Table 1 by first dry-blending the constituents, and then supplying them to a single-screw extruder with a 24:1 length/diameter (L/D) ratio. This extruder comprised 4 heating zones which were maintained at 238°C for zone 1 and 260°C for zones 2 through 4. The pressure in the extruder was 800 psi (5.5 MPa). The extruder was operated to produce approximately 30 lbs/hour (13.6 kg/hour) of the composition; the screw rotational

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speed was approximately 25 rpm. The extrudate exiting the extruder was then force in to conventional film forming die head of the "coathanger" type, which had a die gap of 30 mils (750 μ m), and a width of 14 inches (35.6 cm). The die
5 head was maintained at a temperature of 260°C; the rate of film production was maintained at approximately 35 feet/min (10.7 m/min). The extruded film contacted a casting roll whose temperature was maintained at approximately 160°F (71°C), and a heat set roll maintained at approximately
10 65°F (18°C), both rolls were driven at the same speed. A film having a width of 12 inches (30.5 cm), and a thickness of approximately 2 mils (50 μ m) was produced therefrom.

Control

15

A control film was formed from 100% nylon 6 of about 70 FAV, as indicated in Table 1, following the film forming procedures and specifications of Example 1.

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TABLE 1

5	Examples	Control	1	2	3	4
	FILM CONSTITUENTS (%)					
	Polyamide					
	Nylon 6 (70 FAV) ^a	100	75	80	-	70
10	Nylon 6 (125 FAV) ^b	-	-	-	80	-
	Modifying Agent					
	Admer TM NF500A ^c	-	25	-	-	-
	Admer TM SF700 ^d	-	-	20	20	-
15	Plexar [®] 3342 ^e	-	-	-	-	30
	a. Nylon 6 with less than 1% caprolactam monomer content, which is available from Allied-Signal Inc. as Capron [®] 8207F.					
20	b. Nylon 6 with less than 1% caprolactam monomer content, which is available from Allied-Signal Inc. as Capron [®] 8209F.					
	c. A maleic anhydride modified linear low density polyethylene, of density of 0.92 g/cm ³ and melt index flow rate of 2.0 g/10 min at 190°C, available from Mitsui Petrochemical Industries, Ltd.					
25	d. A maleic anhydride modified polyolefin blended with a thermoplastic elastomer, of density of 0.88 g/cm ³ and melt index flow rate of 1.0 g/10 min at 190°C, available from Mitsui Petrochemical Industries, Ltd. An analytical analysis has shown that the product is comprised of about 68% ethylene, about 25% propylene, about 7% vinyl acetate and less than 1% maleic anhydride.					
30	e. A maleic anhydride graft modified ethylene vinyl acetate copolymer comprising about 18 % vinyl acetate, about 82% ethylene and less than 1% maleic anhydride, available from Quantum Chemical Corp.					
35						

40

The physical properties of the films were evaluated in the machine direction after conditioning the films by placing them in a 50% relative humidity chamber at room temperature for at least 24 hours. The films were tested for various physical properties in accordance with the ASTM D882-83 test protocols. The results of these tests are shown in Table 2.

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TABLE 2

5	Examples	Control	1	2	3	4
	Tensile Modulus ($\times 10^3$, psi)	95.3	56.6	58.4	54.8	61.8
	(MPa)	(657)	(390)	(403)	(378)	(426)
10	Yield Strength ($\times 10^3$, psi)	4.68	3.28	2.3	3.53	3.47
	(MPa)	(32.3)	(22.6)	(16.3)	(24.3)	(23.9)
15	Yield Elongation (%)	12	16	12	15	17
	Ultimate Strength ($\times 10^3$, psi)	19.1	14.5	15.2	16.5	11.8
20	(MPa)	(132)	(100)	(105)	(114)	(81)
	Ultimate Elongation (%)	361	362	383	320	348

25

The above results show that the addition of the modified polyolefins of the present invention to polyamide compositions substantially improves tensile modulus and yield strength without significantly reducing ultimate strength and ultimate elongation, indicating that the resulting films exhibit flexibility and softness without substantially reducing other desired physical properties.

30

Example 5

35

A film composition comprising 85 weight % nylon 6 of about 125 FAV and 15 weight % Admer SF700 modified polyolefin was further modified by the addition of copper ion, in the form of a copper iodide, potassium chloride blend, to 120 ppm level for heat-stabilization. The composition was extruded as in Example 1 which was then formed into films by forming a bubble of film. The bubble was then drawn in the direction of extrusion while maintaining an internal bubble pressure sufficient to keep

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the bubble in a substantially cylindrical shape with the wall thickness of approximately 2 mils (50 μ m). The pre-heat aged and heat aged physical properties of the resulting film (Example 5) were compared with the properties of a nylon 6 film containing a relatively high level of caprolactam monomer that is commercially available to the vacuum bagging industry (Comparative Example C1). Comparative Example C1 contains about 5 caprolactam, compared to only about 0.6% of Example 5. The pre-heat aged films were conditioned in a 50% relative humidity chamber at room temperature for at least 24 hours, and the heat aged films were prepared and conditioned by placing the films in an air circulating oven maintained at a temperature of 350°F (177°C) and a relative humidity of 50% for 4 hours. The physical properties were evaluated in accordance with the ASTM D882-83 test protocols. The results are shown in Table 3.

TABLE 3

Examples	PRE-HEAT AGED		HEAT AGED	
	C1	5	C1	5
25 Tensile Modulus ($\times 10^3$, psi) (MPa)	90.5 (624)	67.3 (464)	-	-
30 Yield Strength ($\times 10^3$, psi) (PMA)	5.39 (37.2)	4.44 (30.6)	9.15 (63.1)	6.31 (43.5)
Yield Elongation (%)	24	31	28	26
35 Ultimate Strength ($\times 10^3$, psi) (PMA)	16.7 (115)	14.4 (99)	13.1 (90)	12.8 (88)
40 Ultimate Elongation (%)	328	335	347	293

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The difference in the pre-heat aged and heat aged yield strength changes between Comparative Example C1 and Example 5 shows that the film made from the polyamide film composition containing the modified polyolefin of the present invention does not stiffen as much as the film composition utilizing caprolactam as the plasticizer during the heat ageing process, thereby retaining its flexibility. As may be readily determined, the yield strength of Comparative Example C1 increased by about 71% after heat ageing, while Example 5 increased by only about 42%.

In accordance with the present invention, pre-heat aged specimens of Example 5 and Comparative Example C1 were tested for their physical characteristics at different humidity environments. A number of samples were placed in a desiccator, in a 50% relative humidity chamber and in a water bath for at least 24 hours at room temperature to obtain 0%, 50% and 100% relative humidity samples, respectively. The samples were tested in accordance with the ASTM D882-83 test protocols. The results are shown in Table 4.

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TABLE 4

5	Relative Humidity	0%		50%		100%	
		C1	5	C1	5	C1	5
10	Tensile Modulus (x 10 ³ , psi)	348.8	258.9	90.5	67.3	51.5	43.7
	(PMA)	(2405)	(1785)	(624)	(464)	(355)	(301)
15	Yield Strength (x 10 ³ , psi)	11.35	8.00	5.39	4.44	3.23	2.67
	(MPa)	(78.3)	(55.2)	(37.2)	(30.6)	(22.3)	(18.4)
20	Yield Elongation (%)	8	8	24	31	39	16
	Ultimate Strength (x 10 ³ , psi)	10.2	12.7	16.7	14.4	13.0	12.7
25	(MPa)	(70.3)	(87.6)	(115.1)	(99.3)	(89.6)	(87.6)
	Ultimate Elongation (%)	327	299	328	335	449	317

30 The above results show that the film produced from the composition of the present invention provides measurably decreased tensile modulus at all humidity levels, indicating improved flexibility over the film of the prior art. Furthermore, the ultimate elongation and ultimate strength properties of the film of the present invention are not as sensitive to humidity as the films of the prior art, indicating that, unlike the films of the prior art, the films of the present invention provide much more consistent and predictable properties of flexibility and softness at all varying levels of humidity.

It can be seen from the above examples that the films and the film compositions of the present invention provide improved flexible, soft films that have relatively high

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heat stability and low moisture sensitivity. In addition, the film compositions of the present invention do not contain any significantly volatile constituents and can easily be processed to form uniform films due to their non-
5 separating homogeneous blending characteristic.

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What is claimed is:

1. A flexible film comprising, based on the total
5 weight of the film composition, from 50 to 95 weight
percent of a polyamide and 5 to 50 weight percent of a
modified polyolefin having a functional moiety selected
from the group consisting of unsaturated polycarboxylic
acids and acid anhydrides, wherein the tensile modulus of
10 said film is below 580 MPa at 50 percent relative humidity.

2. The flexible film according to claim 1 wherein said
polyamide is selected from the group consisting of nylon 6,
nylon 6/6, and copolymers and blends of nylon 6 and nylon
15 6/6.

3. The flexible film according to claim 1 wherein said
polyamide is nylon 6.

20 4. The flexible film according to claim 1 wherein said
modified polyolefin comprises a poly(α -olefin) polymerized
from α -olefins having 2 to 6 carbon atoms and 0.001 to 10
weight percent, based on the total weight of said modified
polyolefin, of a functional moiety selected from the group
25 consisting of unsaturated polycarboxylic acids and acid
anhydrides.

5. The flexible film according to claim 4 wherein said
poly(α -olefin) is selected from the group consisting of low
30 density polyethylene, medium density polyethylene, high
density polyethylene, linear low density polyethylene,
polypropylene, polybutylene, polybutene-1, polypentene-1,
poly-3-methylbutene-1, poly-4-methylpentene-1, polyhexene,
and copolymers and blends thereof.

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6. The flexible film according to claim 4 wherein said functional moiety is selected from the group consisting of maleic acid, maleic anhydride, fumaric acid, crotonic acid, citraconic anhydride, and itaconic anhydride.

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7. The flexible film according to claim 4 wherein said functional moiety is maleic anhydride.

8. The flexible film according to claim 1 wherein said
10 modified polyolefin further comprises from 3 to 40 weight percent, based on the total weight of said modified polyolefin, of vinyl acetate.

9. The flexible film according to claim 1 wherein said
15 modified polyolefin further comprises a thermoplastic elastomer selected from the group consisting of ethylene/propylene, ethylene/1-butene, butyl rubber, butadiene rubber, styrene/butadiene, ethylene/butadiene, isopropene rubber, and isobutylene rubber.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 92/04807

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl.5	C 08 L 77/02	C 08 L 77/06
(C 08 L 77/02	C 08 L 51:06)	(C 08 L 77/06
		C 08 L 51:06)
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl.5	C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0002761 (BAYER) 11 July 1979, see claims; examples ---	1-9
Y	EP,A,0403109 (MITSUBISHI) 19 December 1990, see examples; claims ---	1-9
Y	WO,A,9107467 (EXXON) 30 May 1991, see claims; abstract -----	1-9
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>^o Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25-09-1992	12. 10. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	A. LEROY	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9204807
SA 61369

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 06/10/92
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		DE-A- 2801585	19-07-79
		CA-A- 1121541	06-04-82
		JP-A- 54100454	08-08-79
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